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Mode of Action of Resins in Preventing Microbial Degradation of Cellulosic Textiles

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MODE OF ACTION OF RESINS IN PREVENTING MICROBIAL DEGRADATION OF CELLULOSIC TEXTILE

by

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13. ABSTRACT

The mode of action of resins in preventing microbial degradation of cotton cellulose has been investigated using polymer forming fire retardants. Compounds were selected that either react chemically with cellulose or polymerize within cotton fibers without any appreciable linkage between resin and cellulose. With these compounds it was possible to test whether resins mechanically block cellulolytic enzymes through formation of a polymeric barrier at a supra molecular level or whether chemical linkage between the polymer and cellulose is necessary at the molecular level to block susceptible sites on the cellulose molecule. Using enzyme degradation and soil burial techniques, it was shown that both forms of resins protect cotton cellulose in the form of sateen fabric or as cotton sliver. Optimum protection, however, is achieved by those resins that react with cellulose with the non reactive resin giving limited protection. Data from ball milled fabric and cotton sliver suggest that even in the case of the non reactive resins there may still be some chemical interaction that contributes to the overall protective mechanism.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
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Microbial Degradation						
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Enzyme Degradation						
Tests						
Resistance						

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2. Food Laboratory

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FOREWORD

The body of this report was originally presented as a paper at the 2nd International Biodeterioration Symposium held in Lunteren, The Netherlands, 13th-18th September 1971. Due to budgetary limitations, a severely condensed account of the presentation was necessarily published in the Proceedings of the Symposium entitled **Biodeterioration of Materials**, Vol. 2, 1972, edited by A. Harry Walters and E. H. Hueck-van der Plas, Applied Science Publishers LTD (London), p. 268-278. In the view of the authors, the condensed version prepared by the editors omits experimental data, illustrations, and discussion essential to a complete documentation of the research effort. This technical report has therefore been prepared to offer readers a full account of the work of the authors as presented at the Symposium.

We are grateful to Norbert Berard and Elwyn T. Reese of the U. S. Army Natick Laboratories for their helpful suggestions and comments, to George L. Drake, Jr. of the Southern Regional Research Laboratory, U. S. Department of Agriculture, New Orleans, La., for providing us with treated materials for study, and to Mary L. Rollins and Ines V. deGruy, also of the Southern Laboratory for photomicrographs of the test materials. We appreciate the efforts of Clarence J. Pope of the Natick Laboratories in carrying out tensile strength determinations on the cotton sliver fibers.

The work was accomplished under project number 1T062713A031.

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MODE OF ACTION OF RESINS IN PREVENTING MICROBIAL DEGRADATION OF CELLULOSIC TEXTILES

1. INTRODUCTION

The use of resins (polymer forming compounds) to protect cellulosic textiles from microbial degradation has been extensively studied during the past decade. Among the resins, triazine compounds, particularly trimethylolmelamine, have interested research workers in the United States and Switzerland. (Berard, Gautreaux, and Reeves, 1959; Berard, Leonard and Reeves, 1961; Ruperti, 1961; Kempton, Rogers and Kaplan, 1963, Kempton and Kaplan, 1964; Hitz, Aenishänslin and Bigler, 1967).

Trimethylolmelamine protects cellulose by preventing cellulolytic enzymes from reaching susceptible sites on the cellulose molecules rather than exerting any toxic action against cellulose degrading microorganisms. Indeed, when trimethylolmelamine is used for treatment of textiles, it is necessary to use a fungicide to prevent surface mildewing despite the fact that the treated fabric is not functionally damaged (Kempton and Kaplan, 1964; Hitz, Aenishänslin and Bigler, 1967). Although the general mode of the protective action of trimethylolmelamine is thus evident, the specific mechanism has not been clarified. A question exists as to whether the protective mechanism is due to chemical linkage between cellulose and trimethylolmelamine forming a barrier at the molecular level or whether the resin forms a polymer that coats and infiltrates cellulose fibers setting up a purely physical barrier. Since trimethylolmelamine is both reactive with cellulose (Willard, Turner and Schwenker, 1965, 1966) and polymer forming (Berard, Gautreaux and Reeves, 1959; Berard, Leonard and Reeves, 1961) either or both situations could exist. Investigators have generally favored the chemical reaction theory (Berard, Leonard and Reeves, 1961; Kempton, Rogers and Kaplan, 1963; Gagliardi and Kenney, 1968) although Berard et al, 1959, originally ascribed the protective mechanism to penetration of cotton by monomeric methylolmelamine which subsequently polymerized around fibers. The concept of protection being afforded by a polymerized coating on the surface of a textile without penetration into the inner fibers has not received any support.

Marchessault and Coalson (1967), in a study for our laboratory, in attempting to define the physical factors affecting enzyme activity on cellulose, investigated enzymatic hydrolysis of four cellulosic substrates (cotton and three regenerated cellulose gels) which differed in crystallinity and degree of swelling. Using enzyme preparations from **Trichoderma viride**, which contains both the C_1 and C_x cellulase factors and from **Pestalotiopsis westerdijkii**, which contain primarily C_x with very little C_1, they concluded that degree of swelling is more important than degree of crystallinity in determining resistance of cellulose to enzymatic hydrolysis. An increase in degree of swelling favored enzyme activity. Micropore size of the gels was directly related to degree of swelling and controlled accessibility of cellulose to cellulase enzymes. They presented a hypothesis involving different "critical pore sizes" which must be present to allow the different sized enzymes to penetrate the substrate and hydrolyze the internal structure. The **T. viride** enzyme complex was hydrolytically effective at smaller pore sizes of substrate than **P. westerdijkii** enzyme. When gels were treated with trimethylolmelamine by the wet fixation technique of Ruperti (1961) Marchessault and Coalson concluded that the results supported the "critical pore sizes" hypothesis since less resin was required to protect the substrate against enzyme of **P. westerdijkii** than from enzyme of **T. viride**. Electron micrographs of thin cross-sections of resin-treated gel showed the large pores as preferred locations for the resin. On the basis of these studies, they concluded that the protective action of resin was one of pore blockage.

Studies with other polymeric systems having a bearing on the mode of action of resin systems were reported by Perkins, Drake and Beninate (1969) who investigated the rot resistance of flame retardant finishes applied to cotton fabrics. Five durable flame retardant finishes were evaluated by soil burial. Three of the treatments were heat cured and two were chemically fixed. The heat cured treatments were tris(1-aziridinyl)-phosphine oxide (APO), tetrakis(hydroxymethyl)phosphonium chloride (THPC), tetrakis-(hydroxymethyl)phosphonium chloride plus methylolmelamine (THPC-MM), and tetrakis-(hydroxymethyl)phosphonium hydroxide plus methylolmelamine (THPOH-MM). THPOH is a reaction product of THPC and NaOH and is believed to be a mixture of THPOH, tris(hydroxymethyl)phosphine (THP), and possibly other methylol phosphorus compounds.

The chemically fixed compounds were THPC-urea-NH_3 and THPOH NH_3. The heat cured treatments form insoluble polymers within the cotton fiber but are also reactive with cellulose as evidenced by cross linking, among other parameters; the chemically fixed treatments result primarily in polymer formation and are essentially immobile and non reactive with cellulose. The immobilization of polymers in the chemically fixed treatment is brought about in the presence of NH_3 with the formation of a highly soluble polymer (Drake, Beninate, Cooper, Walker and Reeves, (1969). Perkins et al (1969) found that in general the heat cured samples afforded better resistance to degradation during soil burial than chemically fixed ones.

The report of Perkins et al (1969) provided the basis for our present attempt to more clearly define the mode of action involved in resin system protection of cellulose from microbial degradation. Since the chemically fixed THPOH-NH_3 and THPC-urea-NH_3 treatments are said to be non reactive with cellulose any protection afforded to a cotton fabric should be due to polymer formation mechanically blocking enzymes according to the "critical pore sizes" theory of Marchessault and Coalson (1967). Since the heat cured treatments, APO-THPC, THPOH-MM and THPC-MM, afforded greater protection than the chemically fixed treatments it appeared that chemical linkage of the polymer to cellulose was required for optimum protection. The studies described below detail work carried out with the flame retardants APO, THPC and THPOH in both cellulose reactive and non reactive forms to resolve the issue.

2. MATERIALS AND METHODS

Cotton fabric and sliver treated with the various flame retardants were furnished by the Southern Utilization Research and Development Division of the U. S. Department of Agriculture. The fabric was an 8.5 oz. sateen, undyed and dyed olive drab. An undyed sample was treated with THPOH-urea-MM, 20% add on, and dyed samples were treated with THPOH-urea-MM, THPC-urea-MM, and THPOH-NH_3, 14–19% add on for each treatment. Untreated dyed and undyed controls were carried as appropriate. Cotton sliver was used untreated and treated with APO–THPC, 15–16% add on, 1.95% phosphorus (P); THPOH–NH_3, 15–16% add on, 2.90% P; THPC–urea–MM, 10–11% add on, 1.15% P; and THPOH-urea-MM, 9–10% add on, 1.10% P. The NH_3 treatments were chemically fixed, all the others were heat cured.

Soil burial for all samples and tensile tests for the fabrics were carried out as described by Kaplan, et al (1970). Tensile strengths for the sliver samples were determined by the "flat bundle method" on a Pressley cotton fiber strength tester according to ASTM D-1445-67 (1970). Penetration of flame retardants was ascertained through photomicrographs of Kiton Blue V stained sections of the treated materials as described by Drake et al (1969). The stain is taken up by the resin.

Enzyme susceptibility was measured by incubating fabric or sliver with **Trichoderma viride** cellulase (0.5 mg protein/ml, filter paper activity 1.40) at pH 4.8, 50 C and measuring glucose production (Mandels and Weber, 1969; Kaplan, et al, 1970). Cellulosic materials were tested for enzyme degradation as intact samples, after Wiley milling (20 mesh) and after ball milling for 24 hours.

3. RESULTS

Soil burial of the flame retardant treated fabrics (Table 1) confirmed the fact that heat cured THPC and THPOH treatments offered greater protection than the chemically fixed THPOH-NH_3 treatment. Some protection was afforded by the THPOH-NH_3 treatment as compared to the untreated control but this is considered by us to be marginal in effectiveness. Enzyme degradation of the samples (Table 2) agreed with the soil burial results relative to order of susceptibility after the various treatments. When the samples were ground to 20 mesh in a Wiley mill, there was an increase in susceptibility for all treatments as compared to the unground samples with the THPOH-NH_3 yielding significantly greater amounts of glucose as compared to the THPOH-urea-MM and the THPC-urea-MM treatments but less glucose than the corresponding untreated controls. When the Wiley milled samples were further subjected to 24 hours of ball milling, there was a further increase in susceptibility for all samples. For the dyed sateen samples, comparing the THPOH-NH_3 treatment with the THPOH-urea-MM, significantly larger yields

TABLE 1.

Microbial resistance of flame retardant treated cotton sateen during soil burial.

Fabric treatment	Burial time (days) 0		7		14		21		42		63		84	
	BS[a] (lb)	Ret.[b] (%)	BS (lb)	Ret. (%)	BS (lb)	Ret. (%)	BS (lb)	Ret. (%)	BS (lb)	Ret. (%)	BS (lb)	Ret. (%)	BS (lb)	Ret. (%)
undyed sateen THPOH-urea-MM	130	100	-	-	-	-	134	103	136	105	138	106	140	108
OD[c] sateen control[d]	130	100	36	38	11	8	0	0	-	-	-	-		-
OD sateen THPOH-urea-MM	115	100	-	-	-	-	122	106	107	93	116	101	107	93
OD sateen THPC-urea-MM	97	100	-	-	-	-	106	109	98	101	110	113	102	105
OD sateen THPOH-NH_3	132	100	-	-	-	-	48	36	4	3	0	0	-	-

a. Breaking strength.
b. Retention.
c. Olive drab.
d. Undyed sateen.

TABLE 2.

Enzyme resistance of flame retardant treated cotton sateen.

	Fabric treatment	Incubation time (days)	Glucose produced (mg/ml) by enzyme action[a] Unground cotton	Wiley milled	Ball milled
1.	Undyed sateen control	1	6.4	9.7	14.1
		2	10.6	15.1	16.7
		4	14.0	16.6	18.4
2.	Undyed sateen THPOH-urea-MM	1	0.4	1.0	6.4
		2	0.3	1.5	8.5
		4	0.4	1.4	8.8
3.	OD[b] sateen control	1	4.4	6.1	10.1
		2	6.3	10.1	14.4
		4	7.9	12.9	15.9
4.	OD sateen THPOH-urea-MM	1	0.4	1.2	1.3
		2	0.6	1.6	2.1
		4	0.5	1.5	2.4
5.	OD sateen THPC-urea-MM	1	0.2	1.2	1.7
		2	0.3	1.6	2.9
		4	0.3	1.4	3.6
6.	OD sateen THPOH-NH_3	1	1.4	4.6	4.4
		2	2.6	6.3	8.1
		4	3.2	7.4	9.2

a. 500 mg cellulose in 5 ml **T. viride** cellulase solution. Actual sample weights – #1 – 500 mg, #2 – 596 mg, #3 – 500 mg, #4 – 560 mg, #5 – 583 mg, #6 – 512 mg. Incubation temperature 50 C, pH 4.8. Incubation in unshaken test tubes.

b. Olive drab.

of glucose were found for enzyme treatment of the THPOH-NH_3 sample as compared to the homologous THPOH-urea-MM treatment for both Wiley and ball milled samples. The THPOH-urea-MM treated undyed sample showed much greater susceptibility after ball milling than did the similar dyed sample.

When the data are compared with respect to relative enzyme susceptibility of the fabrics (Table 3), the superiority of the heat cured treatments over the chemically fixed THPOH-NH_3 treatment is apparent. With the exception of the ball milled undyed THPOH-urea-MM, none of the treated samples approach the relative susceptibility of the THPOH-NH_3 samples. Comparison of the dyed samples indicates an increase in relative susceptibility of the heat cured samples with milling. The THPOH-NH_3 samples showed high initial susceptibility with the increase coming on Wiley milled samples with no further change on ball milling

The above data can be interpreted to mean that polymer formation alone, i.e. mechanical blocking of pores in a cellulose matrix, and coating of fibers is not the primary mechanism of protection and that chemical linkage between the flame retardants and cellulose is essential for optimum protection. Examination of photomicrographs of cross sections of fabric samples treated with THPOH-NH_3, OD; THPOH-urea-MM, undyed; and THPC-urea-MM, OD, however, did not permit us to draw firm conclusions at this point since the treatment with THPOH-NH_3 (Figure 1), showed penetration only up to about 1/3 the distance from outside to the center of the yarn with considerable deposit between the dyed fibers. Two thirds of the fibers in the yarn were unaffected by the impregnant. Thus, the failure of the THPOH-NH_3 treatment to protect is simply due to an uneven treatment. The THPOH-urea-MM (Figure 2) sample was well penetrated but the treatment was not uniform as indicated by approximately 25% ring-dyed or completely undyed fibers, without appreciable build up of resin between fibers. The entire THPC-urea-MM (Figure 3) yarn is treated but there is a non uniform treatment which however is more uniform than the THPOH-urea-MM sample. The non uniformity of the THPOH-urea-MM treatment could account for the large increase in relative susceptibility of this undyed treated fabric when ball milled (Table 3).

TABLE 3.

Relative enzyme susceptibility of flame retardant treated cotton sateen at 4 days of incubation time.[a]

Fabric treatment	Unground cotton	Wiley milled	Ball milled
Undyed sateen control	100.	100.	100.
Undyed sateen THPOH-urea-MM	2.7	8.5	48.
OD[b] sateen control	100.	100.	100.
OD sateen THPOH-urea-MM	6.9	8.5	15.
OD sateen THPC-urea-MM	3.3	9.0	22.
OD sateen THPOH-NH_3	41.	57.	58.

a. Relative susceptibility $= \dfrac{\text{glucose from treated sample}}{\text{glucose from control sample}}$.

b. Olive drab.

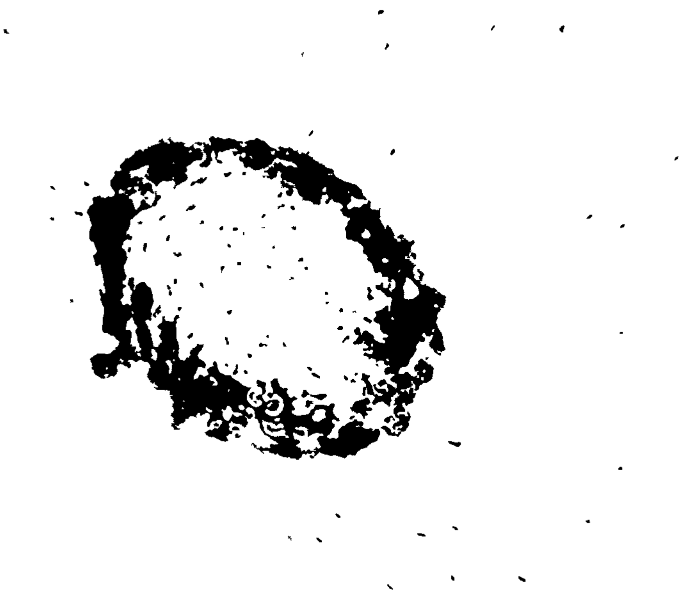

FIGURE 1. Photomicrograph of THPOH-NH_3 treated olive drab cotton sateen. Dark areas show resin pentration. Background circles are cross sections of nylon fiber used to hold the cotton yarn in place during sectioning.

FIGURE 2. Photomicrograph of THPOH urea-MM treated cotton sateen. Dark areas show resin penetration. Background circles are cross sections of nylon fiber used to hold the cotton yarn in place during sectioning.

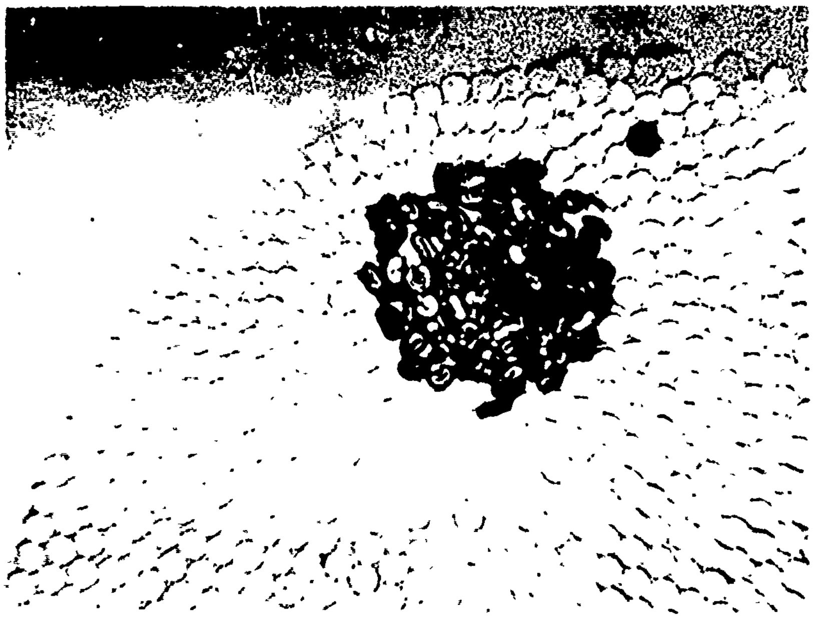

FIGURE 3. Photomicrograph of THPC-urea-MM treated olive drab cotton sateen. Dark areas show resin penetration. Background circles are cross sections of nylon fiber used to hold the cotton yarn in place during sectioning.

FIGURE 4. Photomicrograph of THPOH-NH_3 treated cotton sliver. Darkened areas indicate deposition pattern of the resin.

In order to assure samples of equivalent penetration and thus eliminate uneven treatment as an experimental variable, cotton sliver which could be treated with greater uniformity was chosen for further studies. A photomicrograph of THPOH-NH_3 treated sliver (Figure 4) shows penetration throughout the sample although ring-dyed fibers are evident. Photomicrographs of APO-THPC, THPC-urea-MM, and THPOH-urea-MM showed similar penetration of treatment. Enzyme degradation of treated cotton sliver (Table 4) shows the heat cured APO-THPC more resistant than the THPOH-NH_3 treatment. Wiley milled samples showed some increase in glucose production over unground samples while ball milling increased glucose yield appreciably. Relative enzyme susceptibility of the samples (Table 5) shows the superiority of the reactive APO-THPC over the polymer forming non-reactive THPOH-NH_3 treatment. Relative ranking was maintained for Wiley milled samples but after ball milling, which increased susceptibility quite markedly, the THPOH-NH_3 was less susceptible than the APO-THPC treatment.

Soil burial assay of the samples confirmed the superiority of the APO-THPC treatment over the THPOH-NH_3 treatment (Table 6). The soil burial data however do not fully reflect the greater resistance to microbial attack of the APO-THPC treatment since they represent values of selected fibers that had retained sufficient structure to permit tensile testing. For the THPOH-NH_3 treatment it became increasingly difficult to find such fibers for testing since almost all of the sliver disintegrated between 28 and 56 days of soil burial while the necessary replicates could readily be obtained from the APO-THPC. The difference in structure between the treatments is clearly illustrated in Figures 5 and 6, showing the appearance of the slivers after 4 and 12 weeks soil burial. After 4 weeks (Figure 5) both samples retained their general appearance although the THPOH-NH_3 does show some adherent soil, an early visual indicator of incipient degradation. After 12 weeks (Figure 6) severe degradation for the THPOH-NH_3 is apparent with all of the fluffy characteristics of the sliver having disappeared and no fibers remaining which could be used for tensile testing. When the soil burial experiment was repeated, comparing the THPOH-NH_3 with THPOH-urea-MM and the THPC-urea-MM, Table 7, the reactive heat cured treatments protected the cellulose longer than the polymer forming immobilized THPOH-NH_3 treatment.

TABLE 4.

Enzyme resistance of flame retardant treated cotton sliver.

Sliver treatment	Incubation time (days)	Glucose produced (mg/ml) by enzyme action[a]		
		Unground cotton	Wiley milled	Ball milled
Untreated	1	4.6	6.9	17.6
	3	9.9	15.5	46.8
APO-THPC	1	0.4	0.8	17.6
	3	0.4	1.1	42.8
$THPOH\text{-}NH_3$	1	1.4	2.9	15.9
	3	1.8	4.7	34.4

a. 250 mg sample in 5 ml T. viride cellulase solution. Incubation in unshaken test tubes, 50 C, pH 4.8.

TABLE 5.

Relative enzyme susceptibility of flame retardant treated cotton sliver at 3 days of incubation time.[a]

Sliver treatment	Unground cotton	Wiley milled	Ball milled
Untreated	100.	100.	100.
APO-THPC	2.7	5.7	95.
$THPOH\text{-}NH_3$	12.	24.	77.

a. Relative susceptibility $= \dfrac{\text{glucose from treated sample}}{\text{glucose from control sample}}$.

TABLE 6.

Microbial resistance of flame retardant treated cotton sliver during soil burial.

Sliver treatment	Burial time (days) 0		3		4		5		28		56		84		112		140	
	BS[a] (psi)	Ret.[b] (%)	BS (psi)	Ret. (%)	BS (psi)	Ret. (%)	BS (psi)	Ret. (%)	BS (psi)	Ret. (%)	BS (psi)	Ret. (%)	BS (psi)	Ret. (%)	BS (psi)	Ret. (%)	BS (psi)	Ret. (%)
Untreated	62,600	100	40,000	64	32,200	51	0	0	-	-	-	-	-	-	-	-	-	-
APO-THPC	36,100	100	-	-	-	-	-	-	36,850	102	25,825	72	23,449	65	18,692	52	17,822	49
THPOH-NH_3	46,400	100	-	-	-	-	-	-	43,200	93	24,300	52	0	0	-	-	-	-

a. Breaking strength, pounds per square inch.

b. Retention.

FIGURE 5. Treated cotton sliver after 4 weeks soil burial.

FIGURE 6. Treated cotton sliver after 12 weeks soil burial.

TABLE 7.

Microbial resistance of THPOH·NH_3, THPOH-urea-MM, and THPC-urea-MM treated cotton sliver during soil burial.

Sliver treatment	Burial time (days) 0		28		56		84	
	BS[a] (psi)	Ret.[b] (%)	BS (psi)	Ret. (%)	BS (psi)	Ret. (%)	BS (psi)	Ret. (%)
THPOH·NH_3	51,500	100	49,825	97	34,700	67	specimen degraded	
THPOH-urea-MM	52,750	100	53,600	102	49,290	93	49,180	93
THPC-urea-MM	47,000	100	50,815	108	43,100	93	47,000	100

a. Breaking strength, pounds per square inch.

b. Retention.

4. DISCUSSION

Optimum protection against microbial degradation afforded cellulosic textiles by resins clearly appears to be related to chemical reaction of resins with the cellulosic substrate. Polymer formation within and around fibers offers some protection but is insufficient to impart long lasting protection and does not block enzymic action. The heat cured treatments, THPOH-urea-MM, THPC-urea-MM and APO-THPC, react with cellulose during polymerization and offer the greatest resistance to cellulolytic enzymes and to microorganisms in the soil as compared to the non reactive polymer forming THPOH-NH_3 treatment. In all instances, the reactive treatments maintained greater resistance to enzymatic attack than did the non reactive treatment when Wiley milled. When samples were more finely ground by ball milling, the relationships held both for fabric and sliver specimens with one exception. The APO-THPC sliver showed greater relative susceptibility than the THPOH-NH_3 treated sliver suggesting that the APO-THPC treatment was not firmly linked to cellulose. Photomicrographs showed an even and thorough deposition of APO-THPC resin throughout the sliver thus eliminating uneven deposition as a cause for this apparent reversal in relative susceptibility. In a series of papers from the Southern Regional Research Laboratory, (Roberts, Wade and Rowland (1970), Roberts and Rowland (1970), Rowland, Roberts and Stark (1970)) it was shown that APO by itself does not cross link extensively with cellulose. Reeves and Perkins (1971) in reviewing the subject of flame retardants, however, note that the combined APO-THPC treatment causes loss in tensile strength and an increase in wrinkle recovery of treated fabric, presumptive evidence for cross linking with cellulose. The exact significance of this behavior for the APO-THPC treated sliver after ball milling eludes us at this point, particularly when the unground sliver shows excellent resistance to enzyme activity and soil burial. It is possible that the ball milling caused breaking of the chemical linkages between resin and cellulose.

It is clearly evident that surface coating of yarns with no extensive penetration of resin into and around fibers does not adequately protect the yarn from enzymatic or microbial attack. The relative susceptibility of the peripherally deposited THPOH-NH_3 is initially high compared to the other treatments with both Wiley and ball milling readily exposing the untreated areas to enzymatic breakdown (Table 3). Even though a treatment

may have penetrated throughout the yarn, uniformity of deposition throughout fibers is essential for optimum protection. Ball milling exposes this non uniformity as is evidenced by the data for the undyed sateen treated with THPOH-urea-MM (Table 3) and confirmed by the photomicrograph of this sample (Figure 2). Due to the insoluble and inaccessible nature of cellulose it is always difficult to attain uniform treatment with a chemical agent.

The apparent protective action of the non reactive THPOH-NH_3, although not as great as the reactive treatments, would seem to support the theory that polymer formation does indeed help in mechanically blocking enzymes. There is some question, however, concerning the assumption that the THPOH-NH_3 treatment is completely non reactive. If the treatment is non reactive, then ball milled samples should approach or equal untreated fabric or sliver controls in their susceptibility to enzyme attack. In no instance, has this occurred for the THPOH-NH_3 treatments but it did occur in the case of the APO-THPC treated sliver, discussed previously. As has been pointed out by Kaplan et al (1970), it is conceivable that change in a small percentage of the anhydroglucose units of the cellulose molecule are sufficient to protect the textile from enzymatic breakdown. Earlier, Gagliardi and Kenney (1968) discussing microbial deterioration of textile resin systems noted that the resin methods of producing durable antimicrobial effects in cellulosic materials involve elimination of a small number of cellulosic hydroxyl groups (low degree of substitution) in the accessible region of the cellulose polymer network. They observed that this effect is general to all hydroxyl reactive compounds and does not demand that polyfunctional or polymeric materials need be used nor is cross linking a necessity. The gist of their remarks indicated that ascribing protection to low degrees of substitution is reasonable. Both Drake et al (1969) and Reeves and Perkins (1971) point out the need for close control of processing conditions when applying the THPOH-NH_3 treatment to fabric to prevent evolution of formaldehyde or formation of water soluble products instead of insoluble polymer. It is possible, therefore, that there may be an opportunity during THPOH-NH_3 treatment for a small amount of reactivity to occur between polymer and cellulose to enhance the resistance of the substrate to enzyme activity.

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